5th EEIGM / AMASE International Conference on Advanced Materials Research

MICRO-RAMAN ANALYSIS OF THE MOLECULAR ORIENTATION OF FLEXIBLE POLYOLEFIN FOAMS

M. Antunes, D. Arencón, V. Realinho and J.I. Velasco*

Centre Català del Plàstic - Universitat Politècnica de Catalunya (UPC), Colom 114, 08222 Terrassa, Spain.

* jose.ignacio.velasco@upc.edu

INTRODUCTION

• The use of polyolefin closed-cell flexible foams in the form of sheets with typical thicknesses of 1 to 3 mm is quite widespread in the packaging sector.

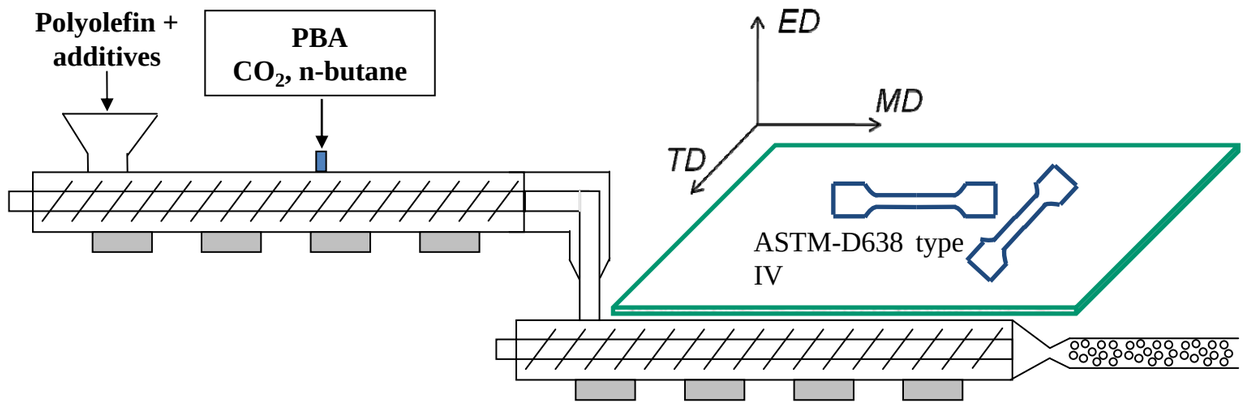
• Although their well-known compressive response, scattered work has been dedicated to the study of their tensile properties regarding the microstructure developed during processing and foaming. Traditionally, X-Ray diffraction techniques have been employed to study the crystal orientation of polymers, with the limitation of using beam sizes up to several millimetres and thus only providing an average value for the whole foam [1-2]. Raman spectroscopy has previously been considered as an alternative [3-4].

• The main aim of this work was to use micro-Raman spectroscopy to determine the crystallinity and orientation level of two polyolefin-based foams, relating the results to their tensile mechanical behaviour.

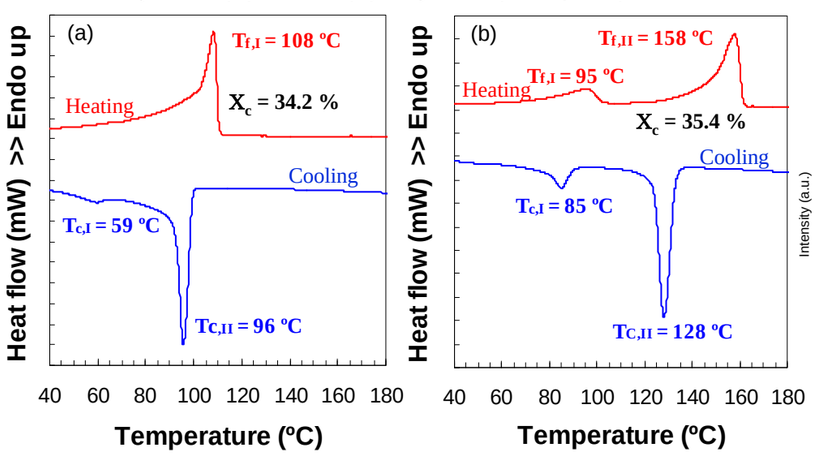
MATERIALS AND EXPERIMENTAL PROCEDURE

• Two commercial 2 mm-thick foamed sheets (*OK Company,* Spain), based on PE and PP and respectively with densities of 20 and 45 kg/m^3, were studied. These foams were produced by a physical foaming process using a tandem extruder, the physical blowing agent (PBA) being added in the first extruder, polymer and gas being progressively mixed and cooled in the second extruder to produce the foamed sheets by sudden decompression at the exit of the extrusion die.

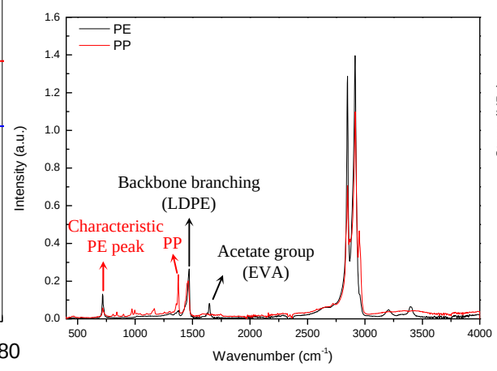
Schematic showing the physical foaming extrusion process and tensile specimen directions:



DSC curves for the (a) PE and (b) PP foams (10 ºC/min):



FT-IR spectra of the PE and PP foams:



MICRO-RAMAN ANALYSIS

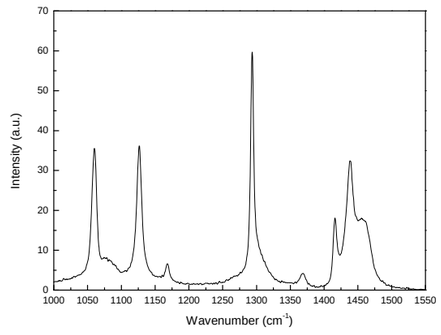
Raman spectra were recorded in a backscattering geometry, using both a ×10 and ×50 microscope objectives, the last one with a spatial resolution of 1 μm^2 (micro-Raman).

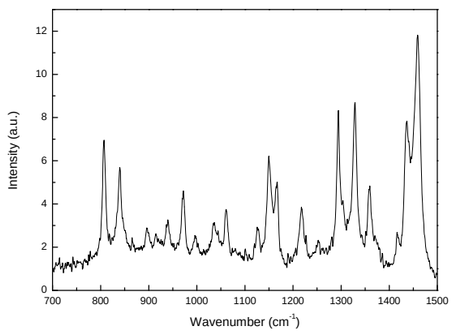
PE's orthorhombic crystallinity [5]:

$$I_{cPE} = \frac{I_{1416}}{(I_{1295} + I_{1305} + I_{1270}) \times 0.45} \times 100$$

PP's α-monoclinic crystallinity [6]:

$$I_{cPP} = \frac{I_{808}}{I_{808} + I_{840}} \times 100$$





Zone	Direction	I_c (%)	I_a (%)	$(I_{1416}/I_{1305})_{norm}$
Edge centre	ED	48.2	9.3	0.9
	TD	53.2	9.5	1.0
	MD	37.9	9.6	0.7
Cell face	ED	45.7	10.9	1.0
	TD	47.4	10.1	1.0
	MD	34.1	9.9	0.8

• Higher crystalline fraction of the chains in the flow direction, leading to a more marked orientation in the edges than in the cell faces.

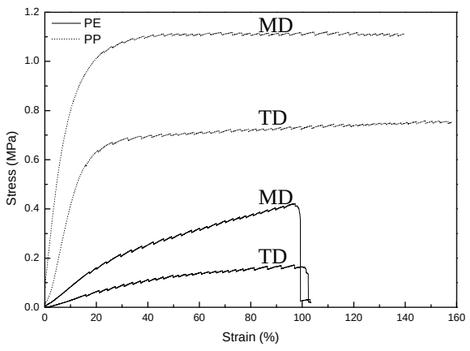
• Higher crystalline fraction for both the edge centre and cell face in TD.

Zone	Direction	I_c (%)	I_a (%)	$(I_{808}/I_{840})_{norm}$
Edge centre	ED	51.9	48.1	0.7
	TD	60.9	39.1	1.0
	MD	58.9	41.1	0.9
Cell face	ED	60.3	39.7	1.0
	TD	59.5	40.5	0.4
	MD	61.2	38.8	1.0

• Slightly higher crystalline fraction of the polymeric chains on the edges in TD than in MD and considerably higher than in ED.

• Measurements performed on the cell face gave almost identical values for the three analyzed directions.

TENSILE BEHAVIOUR

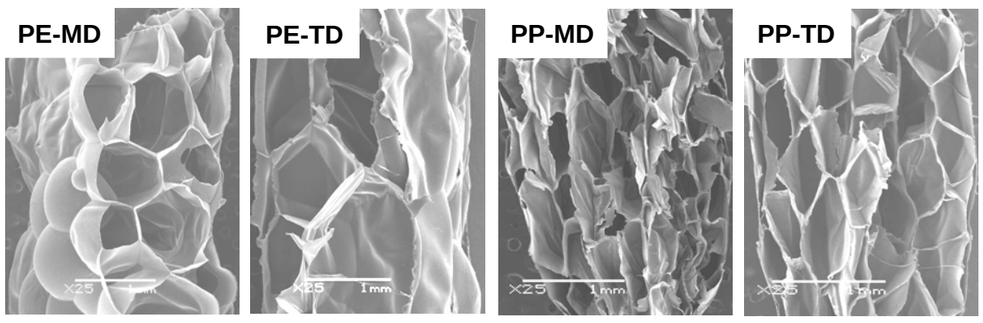


• The predominantly elastic behaviour of the PE foams restricted possible differences related to MD and TD relative crystallinities, the MD specimens showing a higher tensile strength, probably due to predominant cell stretching under these loading conditions.

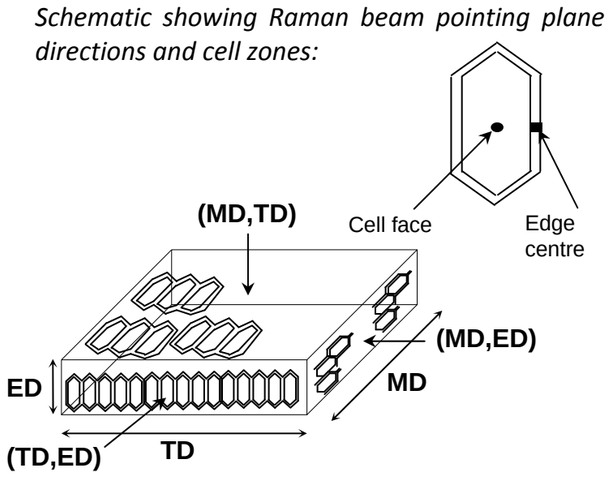
• The combination of a highly MD-stretched material and considerable foaming of the matrix resulted in an MD crystalline-oriented PP matrix, the MD samples showing higher tensile properties than the TD ones.

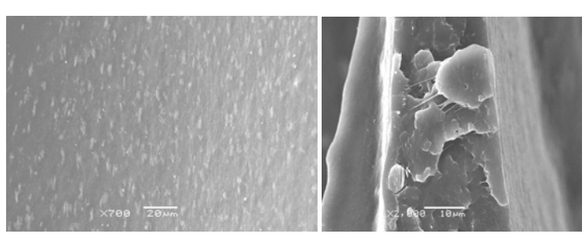
MICROSTRUCTURE AND MORPHOLOGY

• The PE foam presented a more isometric-like cell shape, with aspect ratios (AR) slightly higher than 1, contrarily to the clearly elongated cells of the PP one.



Schematic showing Raman beam pointing plane directions and cell zones:





SEM micrographs showing the presence of an ethylene-based phase in the PP foams

CONCLUSIONS

1. A relative crystalline orientation parameter was proposed considering the most characteristic Raman crystalline peak for PE (1416 cm^{-1}) and PP (808 cm^{-1}) foams.
2. While the PE foams showed a slightly higher TD relative crystalline orientation, the PP ones showed a marked MD orientation, attained to the combined effects of polymer and biaxial stretching during processing and foam growth.
3. Tensile tests showed how the induced MD crystalline orientation of the PP foams resulted in clearly higher tensile strengths than in TD.
4. These preliminary results showed how the knowledge of the inner microstructure is crucial to explain the direction-dependent mechanical properties of the foamed materials.

REFERENCES

[1] Velasco J I, Morhain C, Martínez A B, Rodríguez-Pérez M A, de Saja J A 2002 *Polymer* **43** 6805.
[2] Almanza O, Rodríguez-Pérez M A, Chernev B, de Saja J A, Zipper P 2005 *Eur. Polym. J.* **41** 599.
[3] Rodríguez-Pérez M A, Campo-Arnáiz R A, Aroca R F, de Saja J A 2005 *Polymer* **46** 12093.
[4] Almanza O, Rodríguez-Pérez M A, de Saja J A 2001 *Polymer* **43** 2671.
[5] Ströbl C R, Hagedorn W 1978 *J. Polym. Sci. Polym. Phys.* **16** 1181.
[6] Nielsen A S, Batchelder D N, Pyrz R 2002 *Polymer* **43** 2671.